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Representing Reversible Sinks in Indoor Air Quality Models

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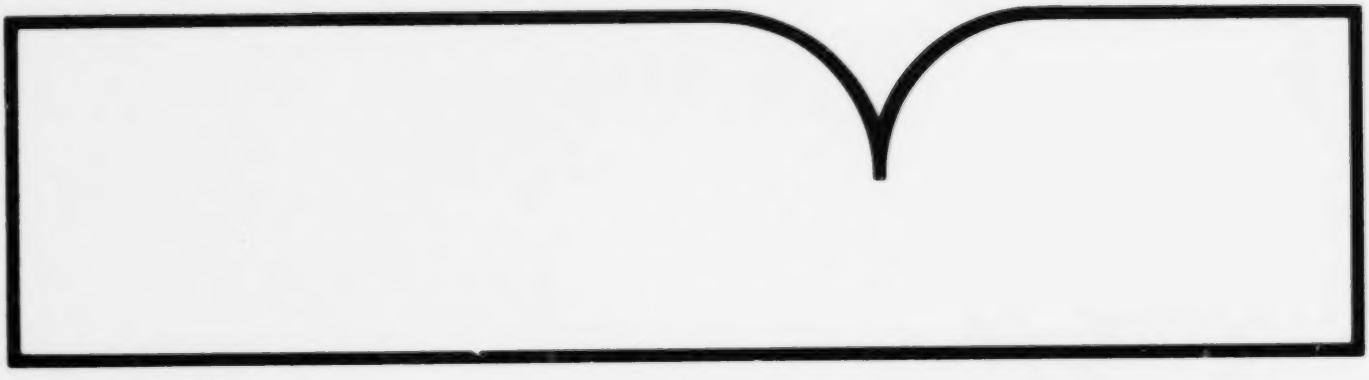

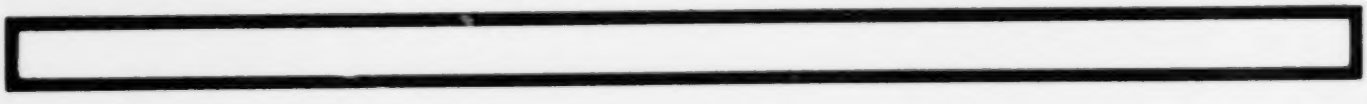

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16. ABSTRACT The paper proposes two models of a reversible sink in an indoor environment. Based on simplified Langmuir assumptions, the kinetic model worked well with flat indoor surfaces such as wallboard, but it failed to predict the long-term, low-level re-emission from complex surfaces such as carpeting. The two-box model takes into account the slow mass transfer process and can be applied to both types of sink materials.

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ON REPRESENTING REVERSIBLE SINKS IN INDOOR AIR QUALITY MODELS

Zhishi Guo[1], James E. Dunn[2], Bruce A. Tichenor[3], Mark A. Mason[1], and Kenneth A. Krebs[1]

[1] Acurex Corp., Environmental Systems Division
P.O.Box 13109
Research Triangle Park, NC 27709, USA

[2] The University of Arkansas
Department of Mathematical Sciences
Fayetteville, AR 72701, USA

[3] U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711, USA

Two models of a reversible sink in an indoor environment are proposed. Based on simplified Langmuir assumptions, the kinetic model worked well with flat indoor surfaces such as wallboard, but it failed to predict the long-term, low-level re-emission from complex surfaces such as carpeting. The two-box model takes into account the slow mass transfer process and can be applied to both types of sink materials.

INTRODUCTION

It has been recognized that reversible sinks play an important role in determining indoor air quality (IAQ) and that an IAQ model has to take them into account in order to make valid predictions of concentrations over time.

Desorption of air pollutants from sink surfaces occurs when the gas molecules are held to the surfaces by relatively weak forces (i.e., van der Waals forces and weak chemical bonds). Adsorption isotherms, such as Langmuir, Freundlich, and BET (Brunauer, Emmett, and Teller), deal only with equilibrium conditions, and are not very useful in predicting IAQ because IAQ models calculate the pollutant concentrations as a function of time. A sink model, therefore, must have the ability to simulate the dynamic processes of adsorption and desorption.

Reports on the study of reversible sinks in an indoor environment are limited. Seifert and Schmahl(1) tested sorption of 21 organic compounds by plywood and carpeting. They concluded that semi-volatile organic substances, such as lindane, are readily retained on textile surfaces, and that, due to subsequent desorption, indoor air concentrations of such substances in normally vented rooms are likely to remain well above normal levels over several days. Dunn and Tichenor(2) first introduced a dynamic sink model with which they tried to compensate for the sink effect in emission test chambers. However, the parameters of their model are dependent on test conditions such as chamber volume, flow rate, and the size of the sink material. More work needs to be done to further characterize reversible sinks, and to develop methods to represent their effects in IAQ models.

THE KINETIC MODEL

In 1918, Langmuir used a simple model of the solid surface to derive an equation for an adsorption isotherm. He assumed that the solid has a uniform surface, that the adsorbed molecules are localized at specific sites, and that

only a monolayer can be adsorbed(3).

Let N be the number of adsorption sites on the bare solid surface of unit area. Let Θ be the fraction of adsorption sites occupied by adsorbate. The rate of desorption, r_d, is proportional to the number ΘN of adsorbed molecules and equals $k_d \Theta N$ where k_d is a constant at fixed temperature. Thus:

$$r_d = k_d \Theta N \quad (1)$$

The adsorption rate, r_a, is proportional to the product of P, the vapor pressure, and $(1-\Theta)N$, the number of unoccupied sites. Thus:

$$r_a = k_a' P (1-\Theta) N \quad (2)$$

where k_a' is a constant at fixed temperature. It was from equations (1) and (2) that Langmuir derived his famous adsorption isotherm.

For most air pollutants in indoor environments, the partial pressures are very low (often in the range from 10^{-12} to 10^{-6} atm). Hence, the fraction of occupied sites, Θ, is a very small number compared to 1. This means that, when dealing with very low pressure adsorbates, equation (2) can be simplified to:

$$r_a = k_a' P N \quad (3)$$

Furthermore, since N is a fixed number for a given solid, it can be merged into ka'. Defining $k_a'' = k_a' N$, then:

$$r_a = k_a'' P \quad (4)$$

Since, in the area of air quality, pollutant contents are often expressed in concentration rather than vapor pressure, equation (4) also can be expressed as:

$$r_a = k_a C \quad (5)$$

where $k_a \propto k_a''$.

Finally, if we let $M = \Theta N$ be the number of adsorbed molecules of certain adsorbate on unity area of the solid surface, then equation (1) becomes:

$$r_d = k_d M \quad (6)$$

We call equations (5) and (6) the kinetic sink model, where k_a and k_d are known as adsorption and desorption rate constants, respectively. In the international unit system, k_a is in m s^{-1} and k_d in s^{-1}. For a specific sink material and air pollutant pair, the two constants are a function only of temperature, and hence independent of such conditions as pollutant concentration, room volume, air flow, and surface area of the sink material. Once their values are determined, they can be applied to real indoor environments. Methods to determine the values of k_a and k_d experimentally are discussed in another paper.

THE TWO-BOX MODEL

Some sink materials, like carpeting, have complex surfaces. The actual processes of adsorption and desorption are far more complicated than the assumptions on which the simple kinetic model is based. For example, it obviously takes longer for molecules diffused deep into the surface to re-emit than those which are adsorbed on the surface in direct contact with the bulk air.

Usually there are two ways to handle complicated cases in modeling: either develop a more complex new model or combine two or more simple models. The two-box model is based on the second approach. In fact, the two-box model is a combination of two kinetic models with different adsorption and desorption rate constants.

To develop the two-box model, we need first to transform the kinetic model into a more intuitive form. It is not difficult to prove that a reversible sink, which follows kinetic equations (5) and (6), is equivalent to, and therefore can be represented by, a box having a certain amount of air exchange with the room. More specifically, for a sink with adsorption rate constant k_a, desorption rate constant k_d, and area S, the volume of the box, V_s, and the air exchange flow, f_s, are determined by:

$$V_s = S\ k_a\ /\ k_d \tag{7}$$

$$f_s = S\ k_a \tag{8}$$

where V_s represents the capacity of the sink, and f_s, the rate of mass transfer.

Since a complex sink may allow mass transfer to take place at different rates, we can put two or more boxes in series. Figure 1 shows a two-box sink model, where (V_1+V_2) represents the capacity of the sink, and f_1 and f_2 represent the rates of fast and slow mass transfer, respectively.

MODELING RESULTS

When the kinetic model is used to represent reversible sinks in an IAQ model, each pair of pollutant and sink material requires one additional differential equation for each room. The system of differential equations describing a chamber or a room with one reversible sink is based on the following material balances: for the pollutant in room air, change in mass = emission - dilution - adsorption + desorption; and for the pollutant in the sink, change in mass = adsorption - desorption. Thus:

$$V\ dC/dt = R_e - f\ C - S\ k_a\ C + S\ k_d\ M \tag{9}$$

$$S\ dM/dt = S\ k_a\ C - S\ k_d\ M \tag{10}$$

or

$$dC/dt = (R_e - f\ C - S\ k_a\ C + S\ k_d\ M)\ /\ V \tag{11}$$

$$dM/dt = k_a\ C - k_d\ M \tag{12}$$

where R_e = emission rate of source;
f = infiltration flow rate;
V = chamber or room volume; and
all other symbols are the same as those in equations (5) and (6).

The kinetic model fit for wallboard/ethylbenzene testing in small chambers is shown in Figure 2. The values of model parameters used are: V=0.0512 m^3, f=0.0499 $m^3\ hr^{-1}$, S=0.14 m^2, k_a=0.63 m hr^{-1}, k_d=2.41 hr^{-1}, R_e=0.566 mg hr^{-1} for the accumulation phase (Figure 2A), and R_e=0 for decay phase (Figure 2B). Also shown is the fit of a "no-sink" model(2).

Figure 3A shows the kinetic model fit for the decay phase of carpet/ethylbenzene testing (V=0.0512 m^3, f=0.0503 $m^3\ hr^{-1}$, S=0.14 m^2, k_a=0.12, k_d=0.20, and R_e=0). As can be seen, the predicted concentration falls below the observed curve as the elapsed time increases. This becomes more obvious in a semi-log plot (Figure 3B). Apparently, if the long-term, low-level re-emission is of concern, the simple model is inadequate.

For the two-box model, each sink/pollutant pair requires two additional differential equations:

$$dC/dt = [R_e - (f + f_1)\ C + f_1\ C_1]\ /\ V \tag{13}$$

$$dC_1/dt = [f_1\ C - (f_1 + f_2)\ C_1 + f_2\ C_2]\ /\ V_1 \tag{14}$$

$$dC_2/dt = f_2 (C_1 - C_2) / V_2 \quad (15)$$

Figure 3B shows the result of fitting this model to the carpet/ethylbenzene data (V_1=0.6, V_2=0.36, f_1=0.11, and f_2=0.008). Since both fast and slow mass transfer processes are available in the model, a much better prediction of long-term, low-level reemissions is obtained.

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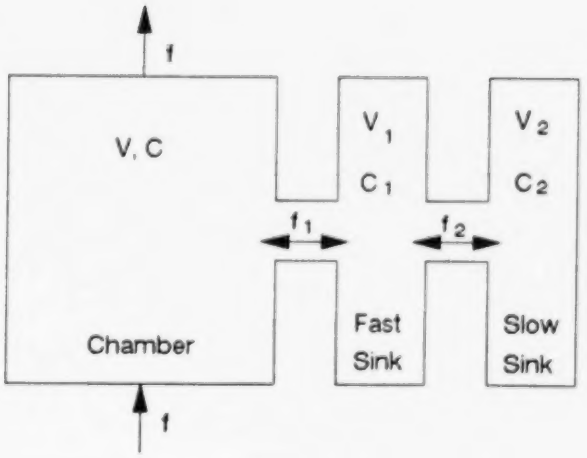

Figure 1. Illustration of Two-Box Sink Model

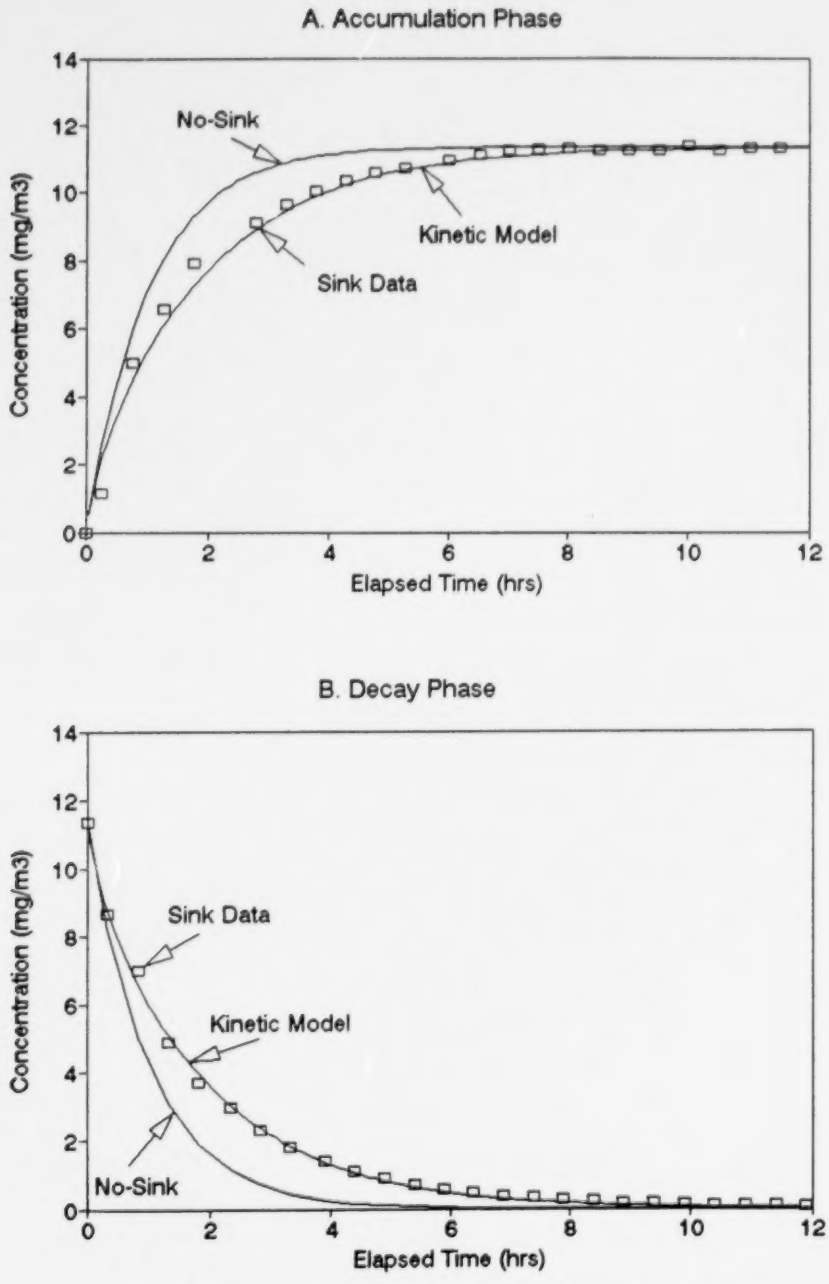

Figure 2. Wallboard as a Sink of Ethylbenzene

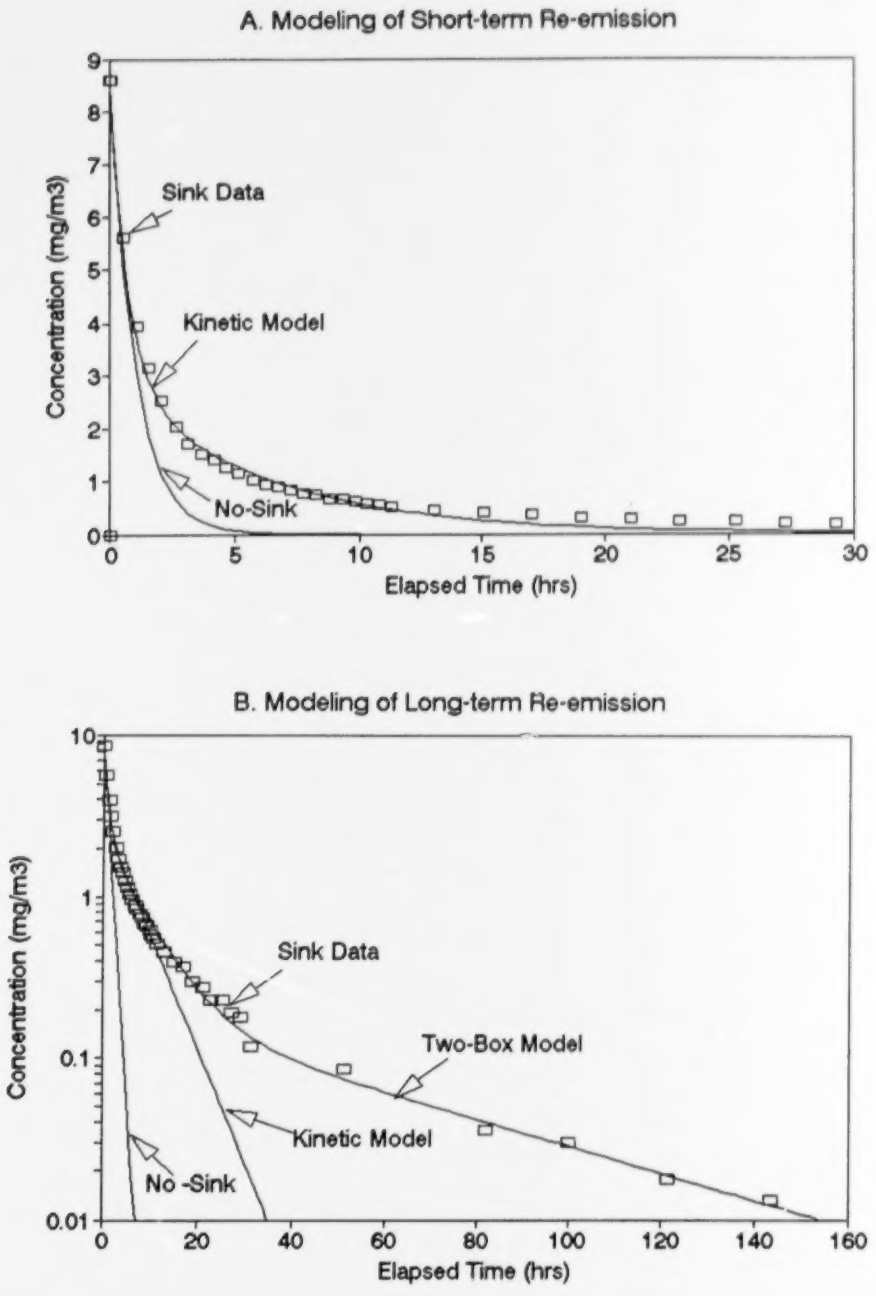

Figure 3. Carpet as a Sink of Ethylbenzene